then triplet excited state valerophenone would have been produced, leading via a Norrish type II cleavage[9] to some acetophenone; no acetophenone was detected by capillary GLPC using authentic standards. Although this failure to detect a dioxetane intermediate as well as that involving styrenyl system **1c** do not prove necessarily that no dioxetane is involved, taken together they suggest strongly that oxidative cleavage of unactivated olefins by $Et_3SiOOOH$ proceeds *mainly* via a nondioxetane pathway.

To account for $Et_3SiOOOH$ acting with electron-rich olefins (e.g., enol ethers) as a dioxetane-forming reagent and with unactivated olefins as a non-dioxetane carbonyl-forming reagent, the mechanism shown in Scheme I is tentatively proposed. This mechanism involves electrophilic $Et_3SiOOOH$[10] undergoing nucleophilic attack by the π-electrons of an olefin with loss of a siloxide ion producing positively charged species having carbocation and/or oxonium ion character; oxonium ion **8** is a protonated perepoxide which can undergo deprotonation via pathway a to produce intermediate perepoxide **9**.[5] Such perepoxides are widely discussed intermediates thought to produce dioxetanes and ultimately two carbonyl cleavage products along with chemiluminescence (CL).[5] Consistent with the intermediacy of perepoxides, some epoxide was indeed observed during $Et_3SiOOOH$ reaction with enol ether **1b**. This mechanistic pathway has some analogy to a mechanism for peracid epoxidation of olefins (i.e., epoxonium ion intermediate).[11] Alternatively, siloxide ion nucleophilic attack at a cationic carbon atom of the initial positively charged intermediate can lead, via pathway b, to *vicinal* peroxy glycol **10**; facile loss of Et_3SiOH with concomitant scission of the glycol unit into two *ground-state* carbonyl fragments would produce neither dioxetanes nor CL. Because *homolysis* of weak peroxidic bonds is a relatively easy process,[5,12] Scheme I could involve radical rather than ionic intermediates.

The results reported here demonstrate for the first time (1) oxidative cleavage of *unactivated olefins* into carbonyl fragments via direct reaction with fresh $Et_3SiOOOH$ (i.e., not via free $^1O_2$ or free O_3) and (2) conclusive evidence for dioxetanes as the major intermediates from direct reaction of nonaromatic *electron-rich olefins* with fresh $Et_3SiOOOH$. These findings raise many mechanistic questions (e.g., ionic and/or radical pathways[13,14]) and synthetic possibilities that we are pursuing.

Acknowledgment. Financial support from the NIEHS (1-PO1-ES-02300) at the early stage of this project is gratefully acknowledged. The NMR spectrometer used in this work was purchased with funds from the NIH (1 S10 RR0934) and from the NSF (DCM-83-03176). T.K. thanks the Nippon Soda Co., Ltd., for a leave of absence and for financial support, and K.S.W. thanks the Lever Brothers Co. for a graduate fellowship. We thank Professor Alex Nickon of this department for helpful suggestions.

Supplementary Material Available: Experimental procedure for oxidative cleavage of methyl oleate (1 page). Ordering information is given on any current masthead page.

(9) (a) Turro, N. J.; Dalton, J. C.; Dawes, K.; Farrington, G.; Hautala, R.; Morton, D.; Niemczyk, M.; Schore, N. *Acc. Chem. Res.* **1972**, *5*, 92. (b) Wagner, P. J. *Ibid.* **1971**, *4*, 168. (c) For a specific example of formation of acetophenone from a valerophenone triplet derived from a dioxetane, see: Turro, N. J.; Chow, M.-F. *J. Am. Chem. Soc.* **1980**, *102*, 5058.

(10) (a) For a review of silyl hydrotrioxides, see: Aleksandrov, Yu. A.; Tarunin, B. I. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 905. (b) For generation of dioxetanes via ozonolysis of vinylsilanes, see: Büchi, G.; Wüest, H. *J. Am. Chem. Soc.* **1978**, *100*, 294. Avery, M. A.; Jennings-White, C.; Chong, W. K. M. *Tetrahedron Lett.* **1987**, *28*, 4629; *J. Org. Chem.* **1989**, *54*, 1789.

(11) Hanzlik, R. P.; Shearer, G. O. *J. Am. Chem. Soc.* **1975**, *97*, 5231 and references therein. See also: Plesnicar, B. In *The Chemistry of Functional Groups, Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; pp 521-584.

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(13) Nelson, S. F. *Acc. Chem. Res.* **1987**, *20*, 269.

(14) Plesnicar, B.; Kovac, F.; Schara, M. *J. Am. Chem. Soc.* **1988**, *110*, 217 and references therein.

Synthesis and Consecutive Double Alkylation Reactions of (2-Siloxyallyl)silanes as the Synthetic Equivalent of Acetone α,α'-Dianion[1]

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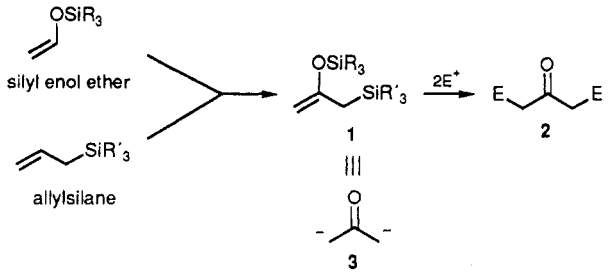
Received February 27, 1989

Summary: (2-Siloxyallyl)silanes as the synthetic equivalent of tandem acetone α,α'-dianion, readily prepared by quenching of the enolate of α-(trimethylsilyl)acetone with chlorosilanes or by 1,3 C→O Si shift of bis(organosilyl)-acetone, react with various electrophiles promoted by a Lewis acid to give the corresponding α,α'-disubstituted acetones.

Sir: Much attention has been focused on the application of organosilicon compounds as synthetic equivalents of reactive intermediates, otherwise inaccessible.[2] Especially allylsilanes and silyl enol ethers are versatile reagents in organic synthesis and have vast potential as a variety of

Scheme I. (2-Siloxyallyl)silane (1) as Acetone α,α'-Dianion Synthon (3)



(1) Studies on Organosilicon Chemistry. 98. For 97, see: Hayashi, T.; Matsumoto, Y.; Kiyoi, T.; Ito, Y.; Kohra, S.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 5667. For 96, see: Hosomi, A.; Kohra, S.; Tominaga, Y. *Chem. Pharm. Bull.* **1988**, *36*, 4622. For 95, see: Hosomi, A.; Ogata, K.; Hoashi, K.; Kohra, S.; Tominaga, Y. *Ibid.* **1988**, *36*, 3736. For 94, see: Tominaga, Y.; Matsuoka, Y.; Hayashida, H.; Kohra, S.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 5771.

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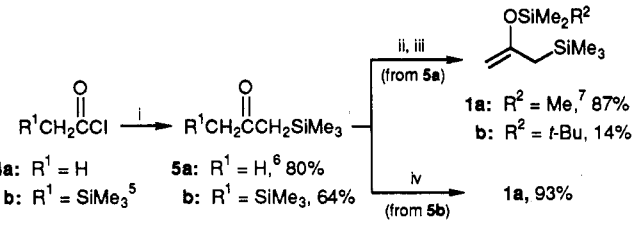
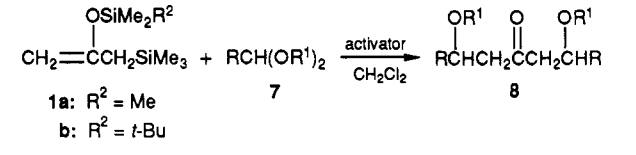
0022-3263/89/1954-3254$01.50/0

Scheme II.[a] **Synthesis of (2-Siloxyallyl)silane (1)**



[a] Reagents and conditions: (i) Me_3SiCH_2MgCl–CuI, Et_2O, −78 °C → rt; (ii) (from **5a**) LDA or $LiN(SiMe_3)_2$, THF, −78 °C; (iii) R^2Me_2SiCl, −78 °C → rt; (iv) (from **5b**) HgI_2, rt.

Table I. Double Alkylations of (2-Siloxyallyl)silanes 1 with Acetals 7



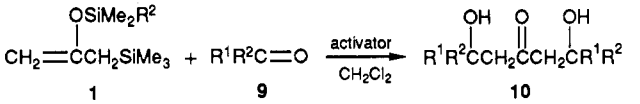
entry	1	acetal 7	conditions[a]	product 8 (% yield)[e]
1	**1a**	$Me_2CHCH_2CH(OMe)_2$ (**7a**)	−78 °C → 0 °C 6.5 h	**8a**[f] (88)
2	**1b**	**7a**	−78 °C → 0 °C 3 h[b]	**8a** (26)
3	**1a**	$BrCH_2CH(OMe)_2$ (**7b**)	−78 °C → −10 °C 9 h	**8b** (49)
4	**1a**	$Me(CH_2)_3CH(OMe)_2$ (**7c**)	−78 °C → 0 °C 5 h	**8c** (64)
5	**1a**	$Me(CH_2)_5CH(OMe)_2$ (**7d**)	−78 °C → −10 °C 3.5 h	**8d** (82)
6	**1a**	$Me(CH_2)_7CH(OMe)_2$ (**7e**)	−78 °C → 0 °C 7.5 h	**8e** (81)
7	**1a**	$PhCH_2CH_2CH(OMe)_2$ (**7f**)	−78 °C → 0 °C 6 h[c]	**8f** (72)
8	**1a**	$PhCH(OMe)_2$ (**7g**)	−78 °C → −10 °C 5 h[d]	**8g** (69)
9	**1a**	p-$ClC_6H_4CH(OMe)_2$ (**7h**)	−78 °C → −10 °C 9 h[d]	**8h** (63)
10	**1a**	$Me_2CHCH_2C(OMe)_2Me$ (**7i**)	−78 °C → 0 °C 4 h	**8i** (46)
11	**1a**	$Me(CH_2)_4C(OMe)_2Me$ (**7j**)	−78 °C → 0 °C 6 h	**8j** (58)

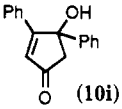
[a] System: **1**, 0.5 mmol; **7**, 2.0 mmol; $TiCl_4$, 2.0 mmol. [b] **1**, 0.5 mmol; **7**, 1.5 mmol; $TiCl_4$, 1.5 mmol. [c] **1**, 0.5 mmol; **7**, 2,0 mmol; $TiCl_4$, 1.2 mmol. [d] **1**, 0.5 mmol; **7**, 2.0 mmol; BF_3·OEt_2, 2.0 mmol. [e] Yield after isolation by TLC. [f] At −50 °C for 18 h, the monoaldol product 4-methoxy-6-methyl-2-heptanone (**11a**) was obtained in 44% yield after hydrolysis without **8a**.

synthetic equivalents of cryptic reactive species that are generally hard to handle and are unstorable.[3] In an extension of the studies on synthons using organosilicon compounds, we have found that (2-siloxyallyl)silanes **1** including skeletons of both an allylsilane and a silyl enol ether are valuable reagents as the acetone α,α'-dianion synthon (**3**) and react with various electrophiles to afford consecutive double alkylation products (**2**) at the α,α'-position of the keto group[4] (Scheme I).

The requisite (2-siloxyallyl)silanes **1** are readily prepared according to the following two methods (Scheme II).

Table II. Double Alkylations of 1a with Carbonyl Compounds 9



entry	carbonyl compound 9	conditions[a]	product 10 (% yield)[d]
1	PhCHO (**9a**)	−78 °C → −10 °C 4 h	**10a**[e] (63)
2	p-ClC_6H_4CHO (**9b**)	−78 °C → 0 °C 5.5 h	**10b** (64)
3	o-ClC_6H_4CHO (**9c**)	−78 °C → 0 °C 8 h	**10c** (65)
4	p-$O_2NH_6H_4CHO$ (**9d**)	−78 °C → 0 °C 2.5 h	**10d** (40)
5	p-MeC_6H_4CHO (**9e**)	−78 °C → 0 °C 9 h	**10e** (54)
6	o-MeC_6H_4CHO (**9f**)	−78 °C → 0 °C 5.5 h	**10f** (68)
7	p-$MeOC_6H_4CHO$ (**9g**)	−78 °C → 0 °C 4.5 h	**10g** (23)
9	$PhCH_2CH_2CHO$ (**9h**)	−40 °C 1 h[b]	**10h** (33)
10	PhCOCOPh (**9i**)	−50 °C → −10 °C 3 h[c]	 (**10i**) (8)

[a] System: **1a**, 0.5 mmol; **9**, 2.0 mmol; BF_3·OEt_2, 2.0 mmol. [b] **1a**, 0.5 mmol; **9**, 1.2 mmol; $TiCl_4$, 1.2 mmol. [c] **1a**, 0.5 mmol; **9**, 0.5 mmol; BF_3·OEt_2, 0.5 mmol. [d] Yield after isolation by TLC. [e] The monoaldol product 4-hydroxy-4-phenyl-2-butanone (**11b**) was obtained in 20% yield, along with **10a**.

Thus, at the outset of the work, an α-silyl ketone (**5**) was obtained by the reaction of an acid chloride (**4**)[5] with [(trimethylsilyl)methyl]magnesium chloride in the presence of cuprous iodide.[6] Then after treatment of **5a** (R^1 = H) with a base followed by a chlorosilane, **1** was obtained in high yield, although the contamination (ca. 10%) of a postional isomer (**6**) in the olefinic part was observed.[7] Alternatively, pure **1a** without **6** can be prepared by the rearrangement of the bis(silyl) ketone **5b** catalyzed by mercuric iodide.[8]

(2-Siloxyallyl)silanes **1**, thus obtained, react with electrophiles promoted by a Lewis acid to give the corresponding double alkylation products **2**. Several examples of the present consecutive double aldol-type reaction with acetals **7** are demonstrated in Table I.[9]

A variety of acetals **7** such as aliphatic and aromatic acetals react with allylsilanes **1** to afford **8** in good yield. Remarkable improvement of the yield was observed when the reaction was carried out in the presence of one or a half equivalent of titanium chloride toward **7** in dichloro-

(3) (a) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200. (b) Majetich, G. "Allylsilanes in Organic Synthesis" in *Organic Syntheses, Theory and Applications*; Hudlicky, T., Ed.; Jai Press Inc.: Greenwich, CT, 1988.

(4) In sharp contrast, it has been found that α,α'-dianions of ketones, obtained by the successive treatments with two different strong bases, undergo only monoalkylation, although they are highly nucleophilic anions. See: Hubbard, J. S.; Harris, T. M. *J. Am. Chem. Soc.* **1980**, *102*, 2110.

(5) Tsuge, O.; Kanemasa, S.; Suzuki, T.; Matsuda, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2851. For the synthesis of (trimethylsilyl)acetic acid, see: Sommer, L. H.; Gold, J. R.; Goldberg, G. M.; Marans, N. S. *J. Am. Chem. Soc.* **1949**, *71*, 1509.

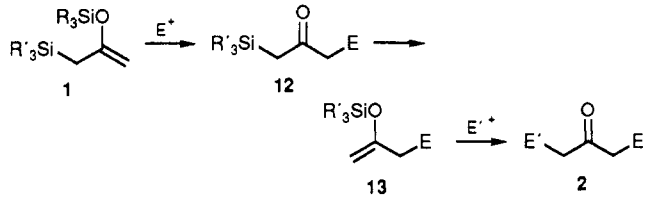
(6) Yamamoto, Y.; Ohdoi, K.; Nakatani, M.; Akiba, K. *Chem. Lett.* **1984**, 1967.

(7) **1a**: ^{1}H NMR (δ ppm in CCl_4) 0.08 (s, 9 H), 0.25 (s, 9 H), 1.53 (s, 2 H), 3.82 (bs, 2 H). **1a** contains a positional isomer, 2-(trimethylsiloxy)-1-(trimethylsilyl)propene (**6**) (ca. 10%). **1b**: ^{1}H NMR (δ ppm in CCl_4) 0.07 (s, 9 H), 0.18 (s, 6 H), 0.93 (s, 9 H), 1.50 (s, 2 H), 3.77 (s, 1 H), 3.82 (s, 1 H).

(8) Lutsenko, I. F.; Bankov, Y. I.; Dudukina, O. V.; Kramarava, E. N. *J. Organomet. Chem.* **1968**, *11*, 35.

(9) A typical experimental procedure is the following. A solution of **1** (0.5 mmol) and an electrophile (2 mmol) in dichloromethane (5 mL) was placed in a flask and cooled to −78 °C with stirring and a Lewis acid (1.2–2 mmol) was added from a syringe. After the mixture was stirred for 5–7 h until the temperature was raised to 0 °C, it was hydrolyzed with saturated $NaHCO_3$. After usual workup, the product was isolated by preparative TLC.

Scheme III. Double Alkylation Reactions of (2-Siloxyallyl)silane (1)



methane. Concerning the reaction temperature and time, the best yield was obtained at −78 °C → 0 °C and 5–7 h. For the aromatic acetals, boron trifluoride etherate is better than titanium tetrachloride as a Lewis acid. In latter case the alkoxy group of the products was replaced by a chlorine atom. With **1b**, the reaction was slow and the yield was rather low.[10]

Reactions of **1a** with carbonyl compounds **9** also gave consecutive double aldol products **10**, although the reactions were rather slow. The representative results are listed in Table II. Although reactions with ketones and aliphatic aldehydes did not always proceed satisfactorily, giving monoaldol products **11** in some cases, **10** was obtained with aromatic aldehydes in respectable yield. Benzyl (**9i**) afforded five-membered ring compounds (**10i**).

In these reactions, the temperature of about 0 °C was required for the occurrence of the second alkylation, presumably due to the slow 1,3 C→O Si shift in **12** under the present conditions.[11] Nevertheless it is well-known that silyl enol ethers react with **7** and **9** even at −78 °C.[12] In addition, since silyl enol ethers are more reactive toward electrophiles than allylsilanes,[2] these facts suggest strongly that the present double alkylation proceeds via a stepwise mechanism as shown in Scheme III, in which **1** works as a silyl enol ether, but not an allylsilane, with an α-silyl ketone (**12**)[13] being formed first. The resulting **12** without isolation undergoes 1,3 C→O Si shift under acidic conditions[6,8,14] to produce a monoalkylated silyl enol ether (**13**), which reacts with another electrophiles to afford a tandem double alkylation product (**2**).

Indeed the synthesis of the unsymmetric ketone **8k** could be realized by the addition of an equivalent of acetaldehyde dimethyl acetal (**7k**) at less than 0 °C followed by **7a**, although the yield was ca. 20%. Moreover, it has been found that the bis(silyl)acetone **5b** can be also viewed as the synthetic equivalent of acetone α,α′-dianion (**3**), although its reactivity is lower than that of **1**, probably due to slow conversion to the incipient **1a** at the stage of the first alkylation.[15]

The synthetic utility of the present reaction was mostly displayed by ready availability of starting materials, which are storable and easy to handle, and simple manipulation of the conversion. The methodology reported here, leading to compounds that are otherwise relatively inaccessible, provides a prototype for other ketone α,α′-dianion equivalents.

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Supplementary Material Available: Preparation of **1** and **5**, reaction procedures of **1** with **7** or **9**, and ^{1}H NMR, IR and MS spectral data for **1**, **4**, **5**, **8**, **10**, and **11** (8 pages). Ordering information is given on any current masthead page.

(10) This might be presumably due to the inefficiency of the nucleophilic assistance toward the silicon atom bearing the bulky *tert*-butyl group by the chlorine or alkoxy group.

(11) See the caption of entry 1 in Table I. Moreover, when the reaction of α-silyl ketone **5a** with **7a** was conducted at 0 °C for 7 h, it was found that 4-methyl-6-methyl-2-heptanone (**11a**) was obtained in 76% yield, although the reaction did not occur at −78 °C.

(12) (a) Mukaiyama, T.; Hayashi, M. *Chem. Lett.* **1974**, 15. (b) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503.

(13) For the fluoride ion promoted and Lewis acid catalyzed reactions of α-silyl ketones, see the following. (a) Fiorenza, M.; Mordini, A.; Papaleo, S.; Pastorelli, Ricci, A. *Tetrahedron Lett.* **1985**, *26*, 787. (b) Johnson, W. S.; Edington, C.; Elliott, J. D.; Silverman, I. R. *J. Am. Chem. Soc.* **1984**, *106*, 7588.

(14) Although the direct conversion of **12** to **2** can not be necessarily excluded, it has been found that the ready 1,3 C→O Si shift occurs at room temperature under Lewis acidic conditions.

(15) Reactions of **5b** with 4 equiv of **7a** and **9b** afforded the corresponding double aldol products **8a** and **10b** in 32% and 38% yields, when reactions were conducted in the presence of $TiCl_4$ and $BF_3{\cdot}OEt_2$, respectively, at −78 °C → 0 °C for 6 h in dichloromethane.

Sulfonate Ester Radical Ion Chemistry

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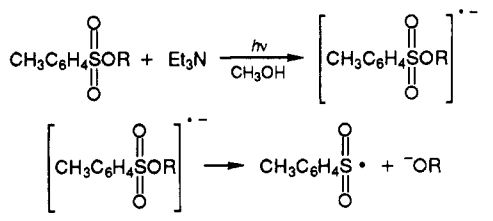
Received April 13, 1989

Summary: Tosylate ester radical anions in the gas phase cleave the sulfonate S–C bond, resulting in formation of a sulfite anion. This is in marked contrast to the solution-phase chemistry, where cleavage of the sulfonate S–O bond to produce a sulfonyl radical and alkoxide ion is observed. The difference in reaction pathways is attributable to solvation of the incipient alkoxide anion leaving group.

Sir: *p*-Toluenesulfonic acid esters, in the presence of an electron donor, undergo photochemical reaction yielding alcohols.[1,2] We have recently demonstrated that photolysis

Scheme I



of these esters initially produces a tosylate ester radical anion, which undergoes heterolytic cleavage to produce a

0022-3263/89/1954-3256$01.50/0